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(54) Title: LIQUID PESTICIDAL FORMULATIONS

(57) Abstract

The invention provides a liquid pesticidal formulation which comprises at least one pesticidal compound, one or more pesticidally acceptable carriers and as a crystallisation inhibitor a) a polyhydroxylated aromatic compound, b) a monohydroxylated aromatic compound, in which the aromatic ring is substituted by halo, alkoxy, nitro, carboxy, cyano or by optionally substituted phenyl in a position ortho to the hydroxy, c) an amino substituted aromatic compound, or d) an aliphatic carboxylic acid of chain length 1 to 8 carbon atoms, comprising one to three carboxy groups, and optionally substituted by hydroxy.

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Title: Liquid Pesticidal Formulations

Field of the invention

This invention relates to novel formulations of pesticides.

Pesticides are commonly formulated as emulsifiable concentrates, in which the active ingredient is dissolved in an organic solvent, such as xylene and mixed with various emulsifying and wetting agents, whereby the resulting concentrate, on dilution with water, forms an emulsion of the pesticide in water which can then be sprayed, e.g. onto crops.

It is now becoming increasingly desirable for environmental, safety and/or cost reasons, that part at least of the organic solvent in such formulations is replaced by water. One way of achieving this would be to have a concentrate comprising the pesticide in a reduced amount of water-immiscible solvent, or even no solvent at all, which is emulsified in water. However, when trying to form concentrates of this type, some pesticides, especially those which are low-melting solids, tend to crystallise on standing and such formulations cannot be re-constituted to give a product of uniform concentration. Thus even if the farmer can remove crystals which would otherwise rapidly clog up spraying apparatus, he is left with a formulation which cannot be applied uniformly to his crop and is therefore wholly unacceptable. This problem is particularly acute with the fungicide having the common name prochloraz, which is N-propyl-N-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide.

In EP 357 559, there are disclosed aqueous formulations of pesticides which have a very low solubility in water. The formulation consists of an aqueous emulsion and contains particular phenols in order to stabilise the emulsion and prevent crystallisation of the pesticide.

We have now found that certain other aromatic compounds and also carboxylic acids are particlarly valuable in inhibiting the crystallisation of a pesticide from a liquid formulation.

Thus, according to the invention, there is provided a liquid pesticidal formulation which comprises a pesticidal compound, one or more pesticidally acceptable carriers and as a crystallisation inhibitor

(a) a polyhydroxylated aromatic compound,

(b) a monohydroxylated aromatic compound, in which the aromatic ring is substituted by halo, alkoxy, nitro, carboxy, cyano or by optionally substituted phenyl in a position ortho to the hydroxy,

(c) an amino substituted aromatic compound,
or

(d) an aliphatic carboxylic acid of chain length 1 to 8 carbon atoms, comprising one to three carboxy groups, and optionally substituted by hydroxy,

and in which the aromatic ring of said aromatic compounds under (a), (b) and (c) is optionally further substituted.

The invention is particularly applicable to oil in water emulsion formulations which also comprise one or more surfactants and/or emulsion stabilisers.

The invention can also be applied to other formulation types, such as microemulsions and emulsifiable concentrates.

The invention also applies to co-formulations. This is particularly applicable to formulations containing two or more pesticidal compounds, in which case, at least one of the pesticidal compounds may be present as a fine particulate solid.

For example an oil in water emulsion of one or more pesticides may be combined with a suspension concentrate of a solid compound suspended in an aqueous medium to give a formulation known as a suspoemulsion.

The pesticidal compound in the formulation of the

tert.-butyl-hydroquinone) and also pyrogallol.

Type (b) compounds are preferably phenols. Halogen substituents are generally chloro. Alkoxy groups are usually of 1 to 4 carbon atoms, e.g. methoxy. Optional substituents include optionally substituted lower alkyl, e.g. of 1 to 4 carbon atoms, especially methyl or t-butyl, carboxy and optionally substituted phenyl. Examples of preferred compounds of this type include 3-methyl-4-nitrophenol and 2- and 3-tert.-butylhydroxyanisole.

The type (c) compound is preferably aniline, optionally substituted e.g. by halo especially chloro, or lower alkyl, e.g. of 1 to 4 carbon atoms, especially methyl. Examples of preferred compounds of this type include 2,3-dimethylaniline and 2-chloroaniline.

Emulsion stabilisers are well known and are generally polymeric products e.g. polyvinyl alcohol/polyvinyl acetate copolymers.

Generally, the formulation also includes a hydrocarbon solvent. Suitable solvents include for example aromatic hydrocarbons such as alkylbenzenes, e.g. xylene, trimethylbenzenes, methylethylbenzenes, dimethylethylbenzenes, diethylbenzenes, tetramethylbenzenes, pentamethylbenzenes, naphthalene and various methylnaphthalenes and mixtures thereof.

If desired, other conventional formulation additives can be included, such as antifreeze e.g. ethylene or propylene glycol.

The composition usually comprises from 30-70%, preferably 40-50%, weight by volume of pesticidal compound; from 5-20% weight by volume of crystallisation inhibitor; from 0-15%, preferably 5-15%, weight by volume of surfactant; 0-10% weight by volume antifreeze; 0-10% weight by volume of emulsion stabiliser; 0-45%, preferably 5-30%, weight by volume of hydrocarbon solvent and 20-40% weight by volume water.

The invention is illustrated in the following examples.

Example 1

Oil in water emulsion formulations were prepared by mixing the following ingredients:

	% w/v	
	A (invention)	B (comparison)
prochloraz	45	45
Mowiol 3-83[1]	2.0	2.0
Genapol C100[2]	2.5	2.5
Hoe-S-3510[3]	3.0	3.0
Proxel XL2[4]	0.2	0.2
Propylene glycol	6.5	6.5
4-methylcatechol	10	0
Solvesso 200[5]	10	20
water	to 100	to 100

[1] = polyvinyl alcohol

[2] = coconut fatty alcohol/ethylene oxide condensate

[3] = alkoxyethylene oxide/propylene oxide condensate

[4] = 1,2-benzisothiazolin-3-one (preservative)

[5] = methylnaphthalene fraction

Samples were stored at various temperatures and the stability of the formulation observed, particularly for crystal formation. To encourage crystal formation, samples were seeded with crystals of prochloraz. After 2 weeks at -5°, 4°C and 8°C, the formulations were examined for crystallisation, by filtering through a 150 micron sieve. Formulation A gave acceptable prochloraz residue levels of 0.015, 0.018 and 0% w/w, whilst formulation B gave unacceptable prochloraz residue levels of 3.0, 0.17 and 0.016% w/w respectively. Even after this short period, it can be seen that the prochloraz crystal residues present

in formulation B would clog spray equipment whilst those in formulation A would not. After 5 weeks storage, the residue levels in formulations A were unchanged whereas those in formulation B had increased further. Both formulations were physically stable, i.e. no breaking of the emulsion had occurred.

Thus even though formulation B comprised more solvent than formulation A, lack of the catechol allowed extensive crystallisation of prochloraz to occur. The presence of the crystallisation inhibitor is thus essential in formulations of this type.

Example 2

Formulations similar to formulation A in Example 1 were prepared in which the 4-methylcatechol was replaced by 5, 10 and 15% tert.-butylhydroquinone and the Solvesso was adjusted to 15, 10 and 5% respectively. The samples were stored at various temperatures and observed for stability of the formulation and particularly for crystal formation. Similar good inhibition of crystallisation and stability of the formulations was observed, as with the formulation A in Example 1.

Example 3

Formulations similar to formulation A in Example 1 were prepared in which the 4-methylcatechol was replaced by acetic acid, citric acid and hydroquinone, respectively. Similar beneficial results were obtained.

Example 4

A suspension concentrate (SC) containg fluquinconazole was prepared by mixing the following ingredients

	% w/v
fluquinconazole	50
Polyfon H[6]	2
Synperonic PE/P75[7]	3
propylene glycol	10.5
Proxel XL2	0.3
xanthan gum	0.2
water to	100

[6] = sodium lignosulfonate

[7] = ethylene oxide/propylene oxide/ethylene oxide block copolymer

This was then combined with an oil in water emulsion formulation prepared from prochloraz and fenpropidin to give a suspoemulsion of the following composition:

	% w/v
prochloraz	20
fenpropidin	18.8
fluquinconazole SC	10.4
Mowiol 3-83	1
Genapol C100	2
Hoe-S-3510	2.5
Proxel XL2	0.075
propylene glycol	5
t-butylhydroquinone	2.2
Solvesso 200	6.7
xanthan gum	0.075
water to	100

This formulation was tested for stability in a similar manner to that described in Example 1 and compared with a

similar formulation in which the t-butylhydroquinone was absent but contained 10% Solvesso 200. After 4 weeks at -5°, the formulation of the invention showed prochloraz residue levels of 0.05% w/w, whilst the formulation contining no t-butylhydroquinone gave unacceptable prochloraz residue levels of 1.4% w/w after only 2 weeks.

Example 5

The fluquinconazole SC described in Example 4 was combined with an oil in water emulsion formulation prepared from prochloraz to give a suspoemulsion of the following composition:

	% w/v
prochloraz	26.7
fluquinconazole SC	13.9
Mowiol 3-83	1.2
Genapol C100	1.5
Hoe-S-3510	1.7
Proxel XL2	0.2
propylene glycol	10.8
t-butylhydroquinone	3
Solvesso 200	8.9
clay thickener	1.6
water to	100

Similar good inhibition of crystallisation and stability of the formulations was observed, as with the formulation of the invention in Example 4.

CLAIMS

1. A liquid pesticidal formulation which comprises at least one pesticidal compound, one or more pesticidally acceptable carriers and as a crystallisation inhibitor
   (a) a polyhydroxylated aromatic compound,
   (b) a monohydroxylated aromatic compound, in which the aromatic ring is substituted by halo, alkoxy, nitro, carboxy, cyano or by optionally substituted phenyl in a position ortho to the hydroxy,
   (c) an amino substituted aromatic compound, or
   (d) an aliphatic carboxylic acid of chain length 1 to 8 carbon atoms, comprising one to three carboxy groups, and optionally substituted by hydroxy,

   and in which the aromatic ring of said aromatic compounds under (a), (b) and (c) is optionally further substituted.

2. A formulation according to claim 1 which comprises water.

3. A formulation according to claim 2 which is an oil in water emulsion formulation and comprises one or more surfactants and/or emulsion stabilisers.

4. A formulation according to claim 2 or 3, which also includes a hydrocarbon solvent.

5. A formulation according to any one of the preceding claims, which comprises prochloraz as a pesticidal compound.

6. A formulation according to any one of the preceding claims, which comprises 30-70% weight by volume of pesticidal compound; from 5-20% weight by volume of crystallisation inhibitor; from 0-15%, weight by volume of surfactant; 0-10% weight by volume antifreeze; 0-10% weight by volume of emulsion stabiliser; 0-45%, weight by volume of hydrocarbon solvent and 20-40% weight by volume water.

7. A formulation according to claim 6 which comprises 40-50% weight by volume of pesticidal compound; 5-15% weight by volume of surfactant and 5-30% weight by volume of hydrocarbon solvent.

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Abstract of **EP0357559**

The invention relates to novel aqueous formulations containing 1 to 70 % by weight of an agrochemical active compound which is poorly soluble in water in addition to an amount of a compound inhibiting the crystallisation of the active substance or a breaking of the emulsion, of the formula I R-O-M (I> in which R denotes C12-C20-alkyl; C12-C20-alkenyl; phenyl; 4-biphenylyl; phenyl which is disubstituted to trisubstituted by alpha -methylbenzyl or alpha -methyl-4-methylbenzyl; or phenyl which is monosubstituted to trisubstituted by alkyl, where the sum of the carbon atoms present in the alkyl groups is 1 to 18; and M is hydrogen; a cation equivalent of an alkali metal or alkaline earth metal ion, or if R is phenyl, 4-biphenylyl or phenyl which is substituted by alpha -methylbenzyl, alpha -methyl-4-methylbenzyl or alkyl can also stand for ammonium, mono- or di-ethanolammonium; and if desired, other formulation auxiliaries and/or other agrochemical active compounds, and their use as seed dressings.